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Impact of Low Ambient Temperature on 3-Way Catalyst Car Emissions

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James N. Braddock
U. S. Environmental Protection Agency
Mobile Sources Emissions Research Branch
Research Triangle Park, NC

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16. ABSTRACT

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ABSTRACT

Regulated and unregulated exhaust emissions from four late model 3-way catalyst passenger cars were measured over the urban dynamometer driving schedule of the Federal Test Procedure as a function of ambient temperature ($50^{o}F$-$81^{o}F$). Fuel economy, regulated emissions HC, CO, NO_x, and unregulated emissions NH_3, HCN, N_2O, CH_4, COS, H_2S, SO_2, SO_4, and C_6H_6 were studied. It was found that reduced ambient temperature operation ($<68^{o}F$) significantly increased the regulated emissions HC and CO, and slightly increased several unregulated emissions. Within the limitations of this study, none of the unregulated emissions were emitted at concentrations that could be considered hazardous to the public.

PREVIOUS STUDIES have demonstrated that ambient temperature affects both exhaust emissions and fuel economy (1-5).* Recent innovations in automotive engineering and exhaust emission control technology (6), however, may have altered both the extent and the manner in which ambient temperature affects exhaust emissions (regulated and unregulated) and fuel economy. The current Federal Test Procedure (FTP) for exhaust emission and fuel economy certification is based on a dynamometer test with a temperature range of $68^{o}F$ to $86^{o}F$ (FTP median temperature = $77^{o}F$). The Department of Transportation has estimated that 66% of all vehicle-miles traveled (VMT) falls below the EPA FTP temperature range, 28% of VMT is within the EPA FTP temperature range and 6% of VMT is above the EPA FTP temperature range (7); in fact, $57^{o}F$ is the actual VMT average-weighted temperature (8) for the continental United States. If ambient temperature variation causes the most recent exhaust emission control technologies to be ineffective outside the 68-$86^{o}F$ FTP temperature window, then the impact of increased exhaust emissions could be quite significant, especially in the colder metropolitan regions of the United States that require transportation control strategies to attain Federally mandated ambient air quality goals.

Thus, in accordance with Section 202(a)(4) of the Clean Air Act Amendments (9), EPA has been directed to investigate both regulated and unregulated vehicle pollutant emission rates and emission rate changes during vehicle operations "outside" of the FTP certification conditions. These investigations are being performed to determine if such non-FTP vehicle operation contributes an unreasonable risk to the public health, welfare, or safety. As part of these investigations, EPA-RTP (Research Triangle Park, N.C.) has measured fuel economy in miles per gallon (MPG), regulated emissions [hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO_x)] and unregulated emissions [individual HC (including benzene, C_6H_6), sulfur dioxide (SO_2), sulfate (SO_4), carbonyl sulfide (COS), hydrogen

*Numbers in parentheses designate References at end of paper.

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sulfide (H_2S), ammonia (NH_3), nitrous oxide (N_2O) and hydrogen cyanide (HCN)] as a function of reduced temperature (50-67°F), below the normal FTP temperature range. Four recent model 3-way catalyst vehicles were tested with both summer and winter grade gasolines in this investigation.

EXPERIMENTAL PROCEDURE

VEHICLE SELECTION -- Four vehicles were used in this investigation: a 1980 Buick Century, a 1980 Chevrolet Caprice, a 1980 Lincoln Continental, and a 1978 Ford Pinto. Vehicle descriptions are provided in Table 1. The Chevrolet, Buick, and Ford were loaned by the manufacturer for use in exhaust emission studies. The Lincoln was new and was leased locally. All test vehicles were conditioned by on-the-road mileage accumulation over a prescribed road route prior to testing. The GM vehicles, designed to meet the 1980 California exhaust emission standards of 0.41 g/mile HC, 9.0 g/mile CO, and 1.0 g/mile NO_x, employed GM's C-4 computer-controlled catalytic converter emissions systems. Major components of this system are an exhaust gas oxygen sensor, an electronic control module (microprocessor computer and input sensors), an electromechanically controlled air-fuel ratio carburetor, and a 3-way catalyst (Buick Century) or a 3-way catalyst plus an oxidation catalyst (Chevrolet Caprice) for reducing HC, CO, and NO_x emissions.

The 1980 Lincoln Continental, designed to meet the 1980 Federal exhaust emission standards of 0.41 g/mile HC, 7.0 g/mile CO, and 2.0 g/mile NO_x, employed central fuel injection (CFI) controlled by Ford's EEC-III electronic engine control system. The EEC-III microprocessor computer and sensors provide fuel control by determining the length of time the fuel injectors are energized. Major components of the EEC-III system include an exhaust gas oxygen sensor, a microprocessor computer, a controlled air-fuel ratio central fuel injection system, and a 3-way catalyst with secondary air injection. The 1978 Ford Pinto was designed to meet the 1978 California exhaust emission standards of 0.41 g/mile HC, 9.0 g/mile CO, and 1.5 g/mile NO_x. It employed a feedback carburetor system for controlling air-fuel ratio, a 3-way catalyst and an oxidation catalyst with air injection for exhaust emissions control. GM's C-4 system and Ford's CFI-EEC-III system are representative of the new wave of sophisticated electronic and mechanical emission control systems that will be used by motor vehicle manufacturers in the 1980's.

TEST FUELS -- Because the overall objective of this study was to determine regulated and unregulated emissions as a function of seasonal variation, two fuel blends, commercial winter and summer grade gasolines, were selected. Use of different gasoline grades for winter and summer temperature driving conditions is typical of actual in-use vehicle operation. Previous studies investigating the effect of temperature on automotive emissions and fuel economy also used separate fuels representative of winter and summer conditions (1,2,4,5).

The winter grade gasoline had a 12.25 psi Reid Vapor Pressure (RVP), a 10% distillation temperature of 109°F, and was used for tests below 68°F. The summer grade gasoline had a 9.45 RVP, a 10% distillation temperature of 126°F, and was used for tests at 68°F and above. These gasoline grades closely resemble the Department of Energy's national average 1979-80 winter grade (12.4 RVP, 10% distillation temperature of 105°F) and national average 1979 summer grade (9.7 RVP, 10% distillation temperature of 120°F) gasoline (10a, 10). Complete fuel specification data are listed in Table 2. The physical property difference(s) between the winter and summer grade gasolines appeared to have little effect on either emissions or fuel economy; temperature variation had the most significant effect (11).

Table 1 - Vehicle Description

Model	Engine	Emission Standard	Inertia Weight	Horsepower Setting	Emission Control Technology
1980 Buick Century 4-door	231 CID V-6 (3.8 L) 2BBL	1980 California 0.41/9.0/1.0	3750 lbs.	11.3	GM C-4 Microprocessor controlled 3-way catalyst, EGR.
1980 Chevrolet Caprice 4-door	305 CID V-8 (5.0 L) 4BBL	1980 California 0.41/9.0/1.0	4000 lbs.	10.3	GM C-4 Microprocessor controlled 3-way catalyst, plus oxidation catalyst, EGR.
1980 Lincoln Continental 4-door	302 CID V-8 (5.0 L) CFI	1980 Federal 0.41/7.0/2.0	4250 lbs.	13.1	Ford EEC-III Microprocessor controlled 3-way catalyst, secondary air, EGR.
1978 Ford Pinto station wagon	140 CID I-4 (2.3 L) 2BBL	1978 California 0.41/9.0/1.5	2750 lbs.	9.9	3-way catalyst plus oxidation catalyst, air injection, EGR.

TEST PROCEDURES

DRIVING CYCLE -- EPA's 1975 FTP or urban dynamometer driving schedule (UDDS) was used for all tests. The FTP is divided into 3 phases: cold transient (CT-bag 1), stabilized (ST-bag 2), and hot transient (HT-bag 3). A 10-minute soak interval is included between the stabilized and hot transient phases, during which time no emissions are generated. A description of the FTP is found in Table 3.

CHASSIS DYNAMOMETER AND FACILITY -- The chassis dynamometer used was a Burke E. Porter No. 1059 electric drive dynamometer with simulated inertias for gross vehicle weights from 1500 to 5500 pounds. Dynamometer control was maintained by a Reliance analog control system. All dynamometer facilities, including the dilution tube, constant volume sampler (CVS), regulated exhaust emissions analyzers, etc., met Federal Register specifications. The CVS diluent air was heated to 115°F to prevent condensation in the dilution tube.

Table 2 - Test Fuel Description

Fuel Property	Winter Fuel	National Average Winter Fuel	Summer Fuel	National Average Summer Fuel
Reid Vapor Pressure, lb.	12.25	12.4	9.45	9.7
Density, grams/cc	0.739	0.735	0.757	0.744
Distillation, °F:				
Initial	76	82	95	89
10 %	109	105	126	120
50 %	225	212	219	223
90 %	357	332	327	336
End Point	412	406	396	411
Paraffins %	64.1	--	48.6	--
Olefins %	6.1	--	7.0	--
Aromatics %	29.8	--	44.4	--
Benzene %	2.36	1.04	2.16	1.07
Carbon %	85.70	--	86.94	--
Hydrogen %	13.62	--	12.21	--
Sulfur %	0.025	0.028	0.014	0.025

Table 3 - FTP Description

Test Phase	Time Duration (Minutes)	Cumulative Distance (Miles)	Cumulative Stops	Cumulative Average Speed (MPH)
Cold Transient (CT - Bag 1)	0.0 - 8.4	3.6	6	25.7
Stabilized (ST - Bag 2)	8.4 - 22.9	7.5	18	19.7
Soak	22.9 - 32.9	7.5	18	19.7
Hot Transient (HT - Bag 3)	32.9 - 41.3	11.1	25	21.3

Note: No measurements are made during the soak phase. Transients are averaged for simulated 7.5 mile distance.

The EPA-RTP dynamometer test cell temperature was dependent upon both the outdoor ambient temperature and the heating/cooling capacity of the large steam-heated and water-cooled heat exchanger used to condition and maintain test cell temperatures. Because of the heat exchanger's thermodynamic limitations, however, the temperature range capability of the test cell was 48°-82°F. Although the span of this temperature range is not great, it does include the 57°F VMT average-weighted temperature. FTP runs in the non-FTP portion of the temperature range (hereafter defined as "subambient" temperature range tests), i.e., below 68°F, could be performed only on days when the outdoor ambient temperature was at or below 40°F. Since the tests were performed during February and March, 46% (19 out of 41 FTPs) were run at temperatures below 68°F; the 54% remainder, (21 of 41 FTPs), were run within the FTP temperature range of 68-86°F (hereafter defined as "ambient" temperature range tests). Test vehicles were soaked in the test cell overnight and the soak temperatures were recorded.

REGULATED AND UNREGULATED EMISSIONS METHODS -- The emissions measurement methods used in this investigation ranged from routine procedures (e.g., those for HC, CO, CO_2, and NO_x) to procedures that required considerable research and qualification before they became operational [e.g., the SO_2 electrochemical method (12)]. A brief summary of both regulated and unregulated analytical methodology is listed in Appendix A. A more complete description of unregulated emissions measurement procedures can be found in reference (13) and in the more detailed EPA report "Analytical Procedures for Characterizing Unregulated Pollutant Emissions from Motor Vehicles" (14). All of the applied analytical methods used, unless otherwise noted, measured diluted exhaust emissions (as opposed to monitoring undiluted raw exhaust emissions) over each test phase of the FTP by either bag sampling, impinger sampling or filter sampling. The SO_2 electrochemical method used an on-line, real time, diluted exhaust sampling procedure; this was the only procedure that measured "real time" response versus "integrated" response.

RESULTS AND DISCUSSION

REGULATED EMISSIONS -- Regulated emissions, HC, CO, and NO_x, are controlled by 3-way catalyst emission control systems which simultaneously oxidize unburned HC and CO to CO_2 and H_2O and reduce NO to N_2. These emission control systems are sophisticated and sensitive devices that require fine control of air-fuel ratio to maintain the low emission levels dictated by the new 1980 California and Federal emission standards. To maintain the proper air-fuel ratio entering the 3-way catalyst, the new emission control systems for 1980 vehicles employ microprocessor-controlled carburetion or central fuel injection. If the microprocessor system should malfunction, the air-fuel ratio could go either rich or lean of stoichiometry depending upon the operating condition of the vehicle. Such a malfunction could result in significant changes in HC, CO, and/or NO_x emissions. Most commonly experienced malfunctions result in an operation that is rich of stoichiometry.

Averages of the various test results for the regulated emissions of HC, CO, NO_x, and fuel economy (MPG) are presented in Table 4. The individual FTP emissions data entries for the Lincoln Continental, the Ford Pinto, and the Chevrolet Caprice are plotted as a function of individual test temperature in Figures 1, 2, and 3. In each figure, the average or mean FTP emission rate for HC, CO, NO_x, and MPG (one for $>68°F$ and one for $<68°F$) are depicted graphically by an "X" located in the center of the emittant's symbol (see figure legend). The dotted lines surrounding the various data entries represent the range of test temperature

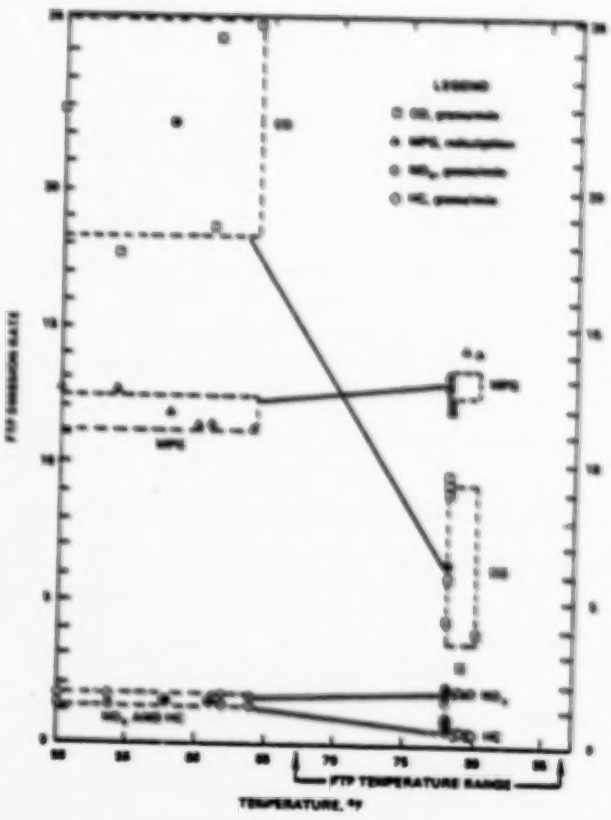

Fig. 1 - 1980 Lincoln Continental FTP emission rate as a function of temperature

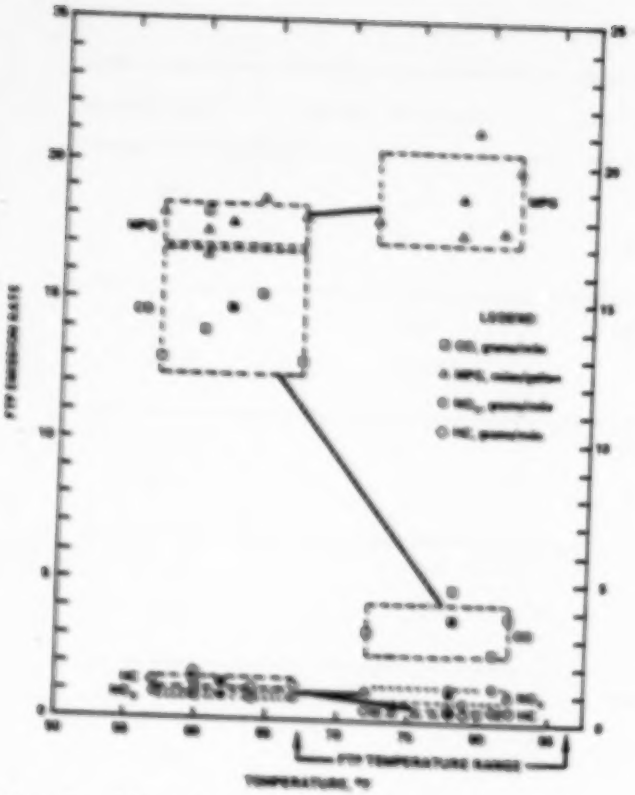

Fig. 2 - 1978 Ford Pinto FTP emission rate as a function of temperature

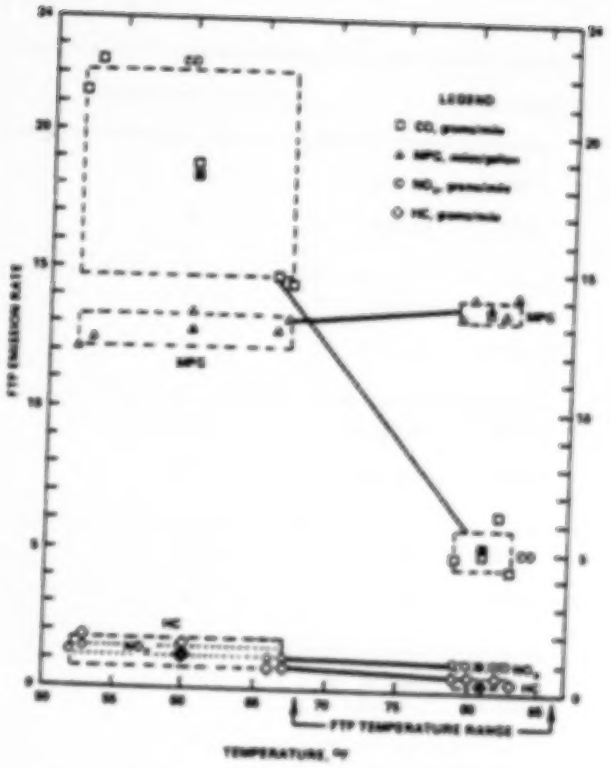

Fig. 3 - 1980 Chevrolet Caprice FTP emission rate as a function of temperature

(x-axis) and 2 standard deviations of the emission mean rate (y-axis). The solid lines connecting the two emissions rate groupings (i.e., one group of runs below 68°F and the other group within the FTP temperature range) depict changes in average emission rates at average test temperature. Data for the Buick Century are not graphically depicted since the microprocessor-assisted emission control system malfunctioned midway through the test schedule. Because the Buick was a 1980 California vehicle, the local GM dealer was, unfortunately, unable to repair it. As a result, the Buick's emission rates exceeded the 1980 California emission standards of 0.41 g/mile HC, 9.0 g/mile CO, and 1.0 g/mile NO_x. These results, then, are not representative of a functional emission control system; however, they are included in Table 4 for malfunction comparison purposes only.

The vehicles with functional emission control systems, the 1980 Lincoln Continental, the 1978 Ford Pinto, and the 1980 Chevrolet Caprice, all met their respective emission standard levels for tests conducted within the FTP temperature range. For tests conducted below 68°F (i.e., subambient), however, HC and CO emissions increased markedly, fuel economy decreased slightly, and NO_x emissions remained about the same. These observations parallel those of other investigators, some of whom examined cars with earlier emission control systems (1-5). The individual bag and overall FTP emissions (composite of bags 1, 2, and 3) are plotted in Figures 4, 5, 6, and 7 for the Lincoln, Ford, Chevrolet and Buick, respectively. In these figures, the average emission rate at the average subambient temperature (58°-62°F) is compared with the average emission rate at the average FTP-range temperature (78°-81° F). The various emissions, HC, CO, and NO_x, and their probable causes (15) will be discussed and analyzed in the following sections.

HC Emissions -- In general, HC emissions are affected by the properties of the fuel, incomplete engine combustion, and wall quenching effects. Fuel property effects will be discussed in the "Unregulated Emissions -- Total Hydrocarbon Composition" section. Wall quenching effects occur in the combustion process when the flame front moves toward a relatively cool cylinder wall surface. The cool wall slows down and effectively stops the combustion process, leaving a layer of unburned fuel near the cylinder wall surface. The

Table 4 - FTP Regulated Emissions Summary

Emission Type		Lincoln Continental	Ford Pinto	Chevrolet Caprice	Buick Century
78°F	HC g/mi	0.26	0.41	0.33	1.60
<68°F	HC g/mi	1.40	1.33	1.18	1.81
78°F	CO g/mi	6.39	3.54	5.06	22.42
<68°F	CO g/mi	22.34	14.64	18.38	30.96
78°F	NO_x g/mi	1.71	1.00	1.00	0.80
<68°F	NO_x g/mi	1.39	0.92	1.21	1.35
78°F	MPG	13.0	18.9	13.7	15.0
<68°F	MPG	11.9	17.8	12.8	14.8
Average temperature within FTP range		78°F	78°F	78°F	78°F
Average temperature outside FTP range		58°F	62°F	60°F	55°F

amount of quenching varies with cylinder temperature and pressure, cylinder deposits, and the wall temperature itself. If we assume that the test vehicles operated in a consistent manner throughout the tests, then the thickness of the unburned fuel layer is affected only by variations from test to test in the initial cylinder wall temperature.

Incomplete combustion effects may be caused by many variables, including a poor ignition system, low charge temperature, poor charge homogeneity, air-fuel ratio, and a large exhaust residue. Carburetion or fuel injection, choke-on time, atomization at the intake valve, turbulence in the combustion chamber, and engine intake system temperature all affect the fuel distribution and influence air-fuel ratio and charge homogeneity. Since most of these variables were controlled in our tests, it is a reasonable assumption that only those variables that affect the temperature of the engine at start-up are responsible for any incomplete combustion effects. Catalyst temperature also influences incomplete combustion effects in that, until the proper catalyst operating temperature (i.e., catalyst light-off) has been achieved, little oxidation of HC and CO occurs and, hence, excess HC and CO emissions pass uncontrolled (i.e., unoxidized) through the catalyst and exit the tailpipe.

From observations of Figures 4, 5, 6, and 7, it is apparent that HC emissions from the cold transient-bag 1 phase of the FTP are especially sensitive to temperature variation. In the Lincoln Continental, bag 1 HC emissions increased from 0.65 to 5.91 g/mile, an increase of 809%; for the Ford Pinto from 0.85 to 4.87 g/mile, an increase of 473%; for the Chevrolet Caprice from 1.15 to 5.93 g/mile, an increase of 416%, and for the malfunctioning Buick Century from 3.15 to 4.42 g/mile, an increase of 40%. HC emissions were not very sensitive to temperature variation during the stabilized-bag 2 and hot transient-bag 3 phases of the FTP. These are predictable results since both the engine coolant temperature and catalyst light-off temperature of the average vehicle stabilize after about 5 minutes regardless of start-up test temperature (15). Thus during warm-up in the FTP cold transient phase, longer choke-on operation time results in increased HC emissions. During the stabilized and hot transient phases, the choke is off, the necessary catalyst operating temperature is achieved and the engine coolant temperature is constant and stable, resulting in little change in HC emissions with FTP temperature variation.

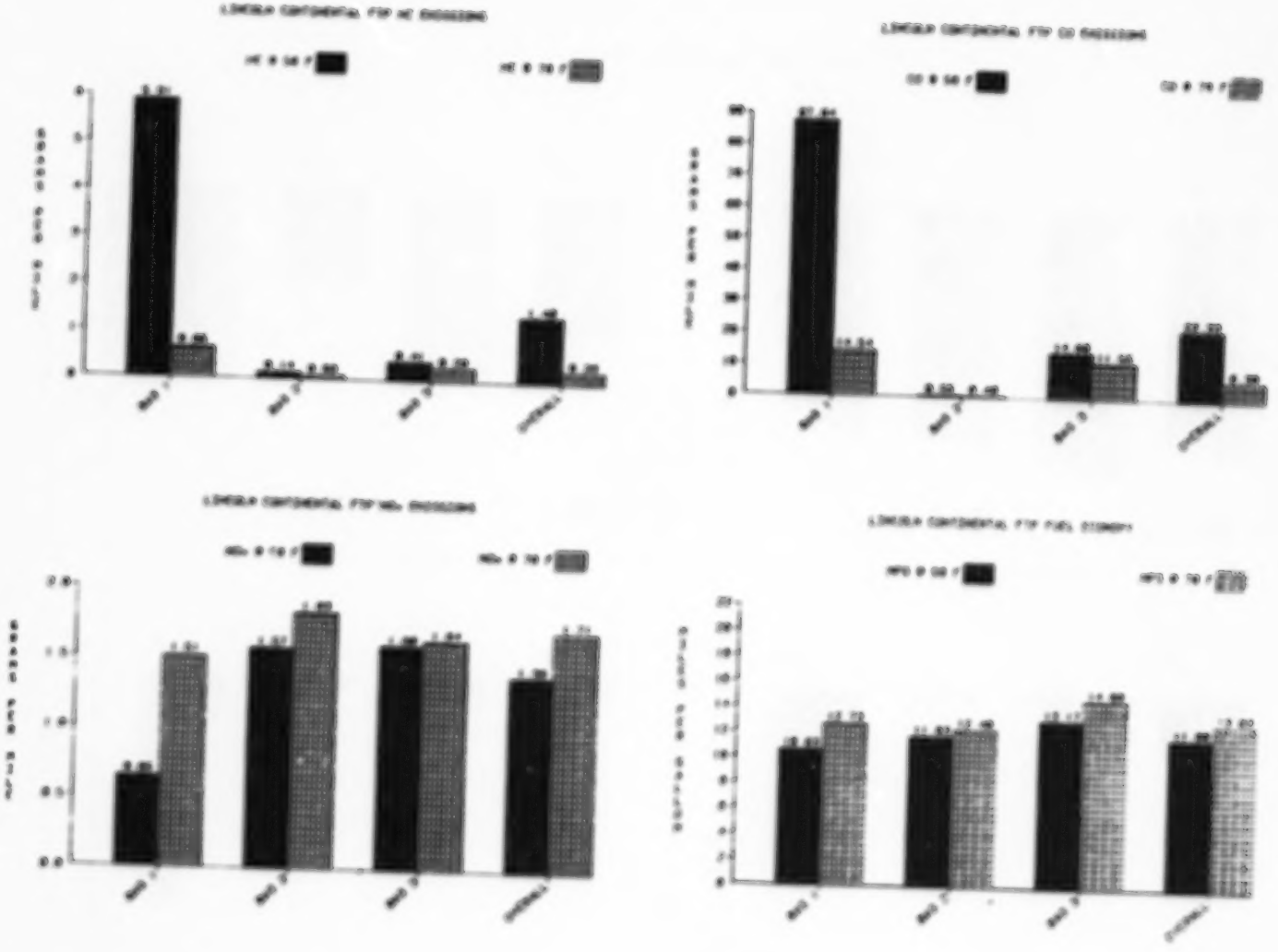

Fig. 4 - Lincoln Continental FTP emissions

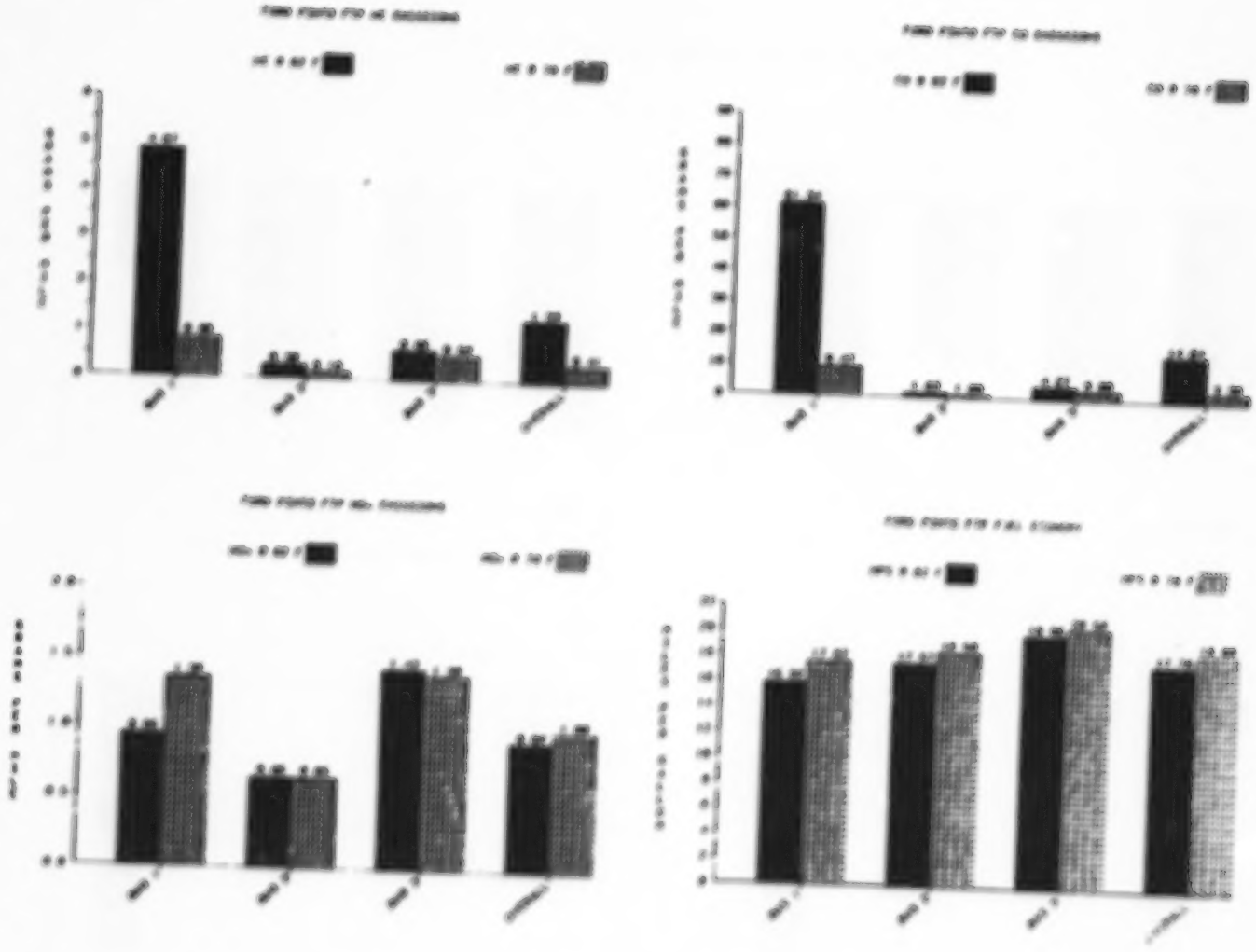

Fig. 5 - Ford Pinto FTP emissions

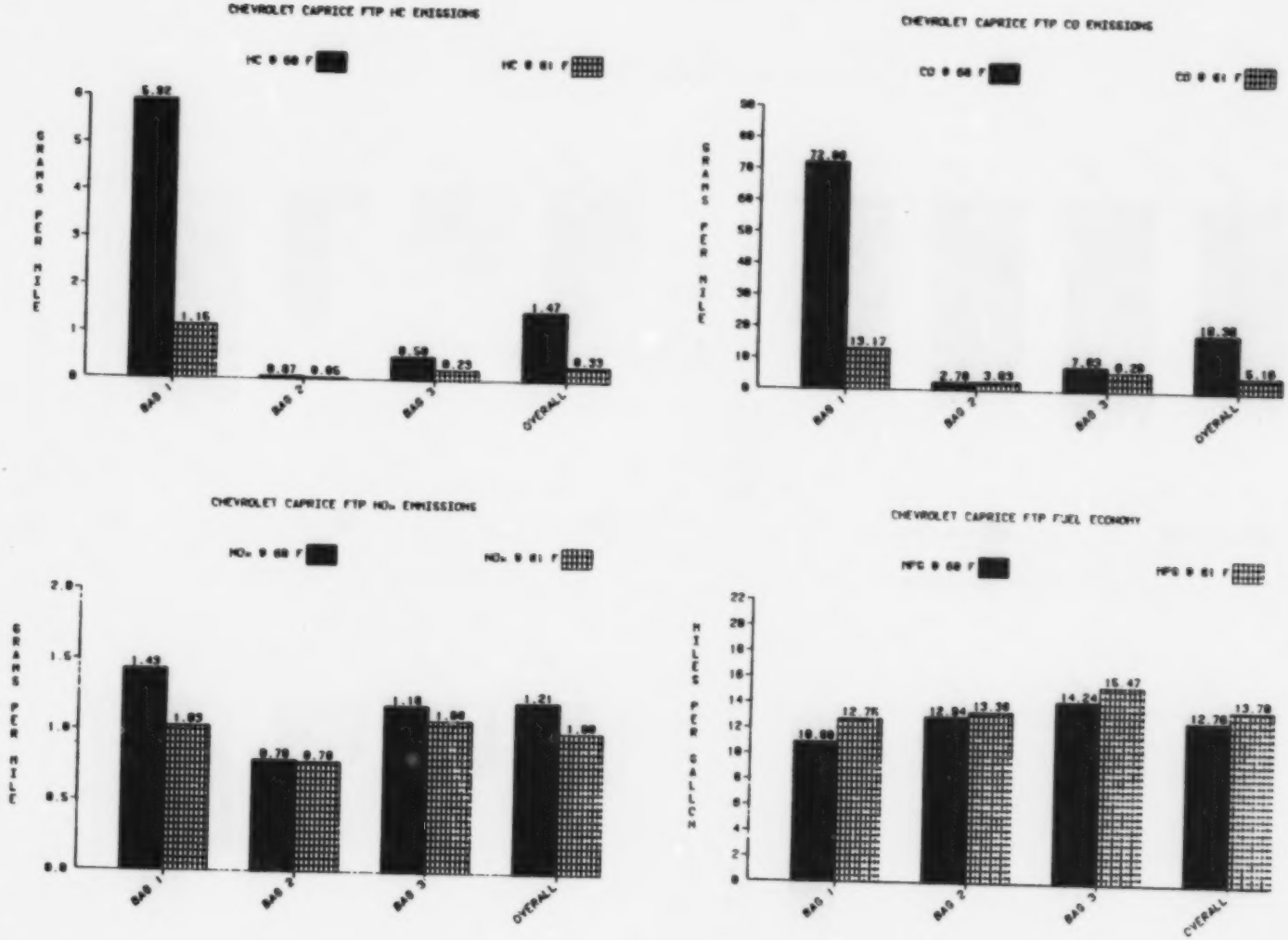

Fig. 6 - Chevrolet Caprice FTP emissions

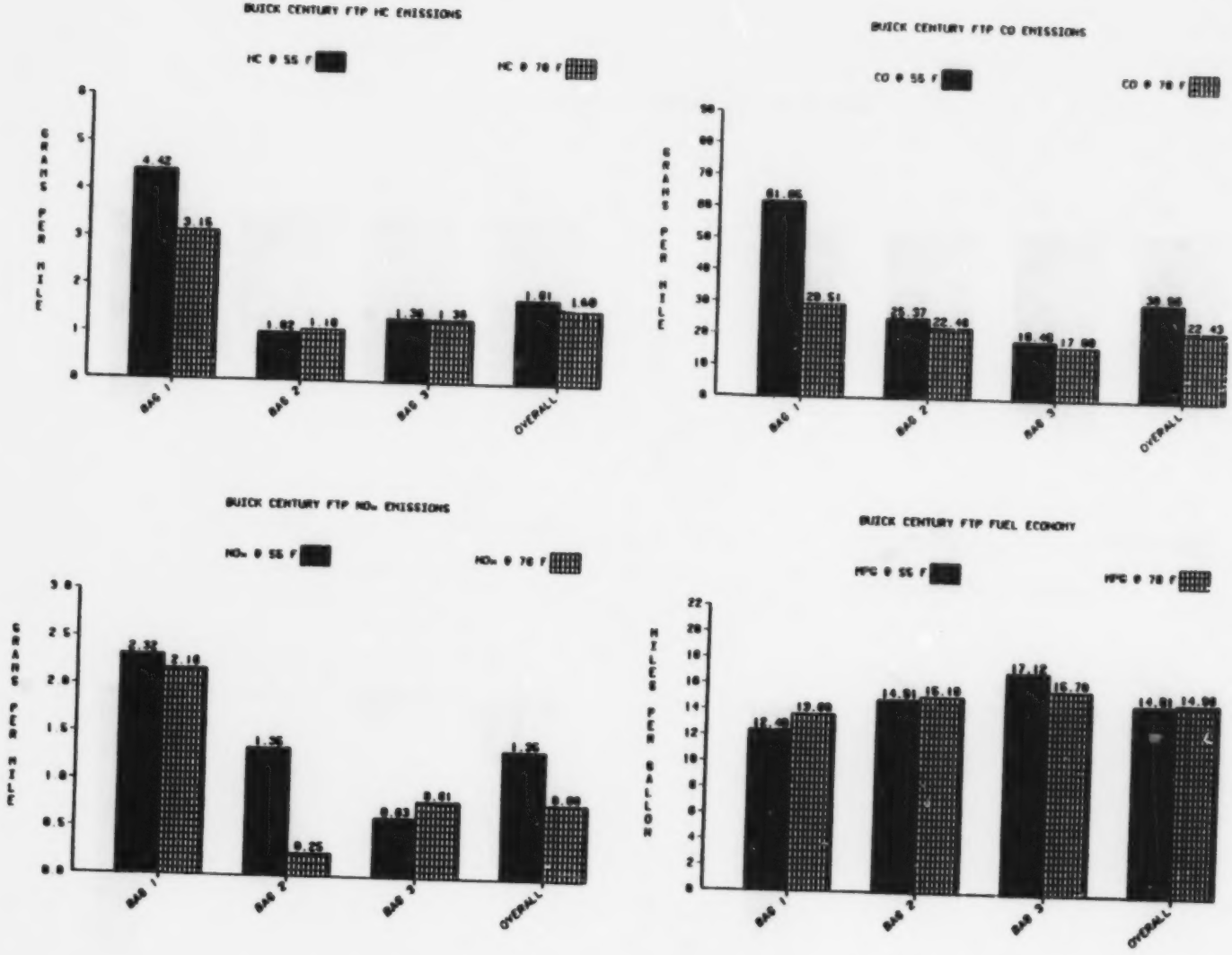

Fig. 7 - Buick Century FTP emissions

Overall FTP HC emissions for the Lincoln, Ford, and Chevrolet test vehicles increased by an average of 307% in the subambient test runs (average cold temperature versus average FTP-temperature emission rates), with almost all of the HC (and CO also) increase occurring during bag 1 vehicle operation, thereby indicating the dominant effect of the cold transient test phase.

CO Emissions -- CO is formed when the air-fuel ratio goes rich of stoichiometry. The most significant rich operating condition occurs during the start-up of a cold engine, since the automatic choke is in operation. The air-fuel ratio usually remains rich from the initial cold start until the engine is warmed to the choke-off temperature. Because the choke-off temperature is preset for each vehicle, the amount of choke-on time then becomes a function of the initial engine start-up temperature. Hence, the colder the start-up temperature, the longer the choke stays on and the longer the air-fuel ratio remains rich, resulting in an increase in CO emissions.

CO emissions displayed a pattern similar to HC emissions: for the Lincoln Continental, the bag 1 emissions increased from 14.54 to 87.64 g/mile, an increase of 603%; for the Ford Pinto, emissions increased from 9.47 to 61.34 g/mile, an increase of 608%; for the Chevrolet Caprice, emissions increased from 13.17 to 72.06 g/mile, an increase of 547%; and for the malfunctioning Buick Century, emissions increased from 29.51 to 61.65 g/mile, an increase of 109%. These large CO emission increases may be attributed to longer choke-on operation times in the subambient temperature tests. Bag 2 and bag 3 emissions of the FTP predictably demonstrated little temperature effect. Overall FTP CO emissions for the Lincoln, Ford, and Chevrolet test vehicles increased by an average of 276% in the subambient runs.

NO_x Emissions -- Nitric oxide (NO) is formed within the combustion chamber at peak combustion temperature and persists during expansion and exhaust in non-equilibrium amounts. NO_x production is maximized at peak combustion temperatures and decreases with decreasing combustion temperature and richer air-fuel ratios. Hence, it would be predicted, assuming all engine variables to be equal or controlled, that NO_x engine-out emissions would decrease as start-up temperatures decrease since the choke-on operation time would be lengthened.

In this study, however, NO_x emissions appeared relatively insensitive to both temperature change and FTP test phase variation. For example, with the Lincoln Continental and Ford Pinto, bag 1 subambient NO_x emissions were less than the 78°F NO_x emissions; on the other hand, with the Chevrolet Caprice and Buick Century, the subambient NO_x emission rate was greater than the 81°F emission rate. NO_x emissions are also a function of the exhaust gas recirculation (EGR) operating characteristics of each engine plus the "width" of the 3-way catalyst window for NO_x control. Another example of the unpredictability of changes in NO_x emissions under various temperature and test phase conditions: Lincoln Continental bag 2 NO_x emissions were never less than either bag 1 or bag 3 emissions; on the other hand, with the Ford Pinto and Chevrolet Caprice, bag 2 NO_x emissions were much less than either bag 1 or bag 3 emissions. Overall NO_x subambient emission rates were similar or equal to the FTP-temperature range NO_x emission rates.

Fuel Economy -- The fuel economy or mileage of a vehicle is dependent upon many variables, including air-fuel ratio, ignition timing, engine temperature, rolling resistance, and frictional losses in the drive train. Since the test vehicles were operated in a consistent manner throughout the characterization program, most of the above variables were controlled or minimized -- except for start-up temperature. It was observed that the MPG rates were sensitive to both temperature change and FTP test phase variation. The individual test phase and the overall FTP subambient mileage figures were always less than the FTP-temperature range figures; the average 19°F temperature reduction decreased the fuel economy by ~7%. Bag 1 subambient fuel economy was always less than either bag 1 FTP-temperature range fuel economy or bag 3 (both subambient and FTP-temperature) fuel economy. Some important reasons for increased subambient HC and CO emission rates and decreased subambient fuel economies are briefly summarized below:

- longer operation time with the choke on for warming up the colder vehicle, thereby resulting in rich air-fuel ratios
- lower thermal efficiency with the colder vehicle as more combustion heat is lost to the combustion chamber walls and coolant, leaving some HC unburned and some CO unoxidized
- longer time periods to reach catalyst light-off temperature (affects emissions only)
- greater friction losses in the engine and drive train of the colder vehicle
- greater rolling resistance due to lower effective tire inflation pressures at reduced temperatures (affects fuel economy only)

- increased aerodynamic drag due to higher air density at reduced temperatures (not a factor in this study)

In summary, it appears that the microprocessor-controlled 3-way catalyst emission control systems function well in the FTP temperature range of 68°-86°F, except for the Buick Century. Below this temperature range, however, these systems display temperature sensitivity. In this study, the average subambient test temperature was 60°F -- only 8°F below the recommended FTP-temperature range minimum of 68°F -- and only 19°F less than the overall average temperature of the FTP-temperature range tests. For the Lincoln, Ford, and Chevrolet vehicles, the 19°F average FTP test temperature reduction resulted in a 307% increase in HC emissions (+16%/°F), a 276% increase in CO emissions (+15%/°F), no net change in NO_x emissions, and a 7% decrease in fuel economy (-0.36%/°F). These results are quite significant: it appears that once ambient temperature drops below the 68-86°F FTP range, the engine operates under a choke-on "best driveability" condition for significantly longer periods of time than when in the FTP temperature range window. This condition results in a rich combustion mixture without adequate catalytic oxidation of HC and CO emissions. Hence, until the vehicle is warmed up and all critical warm-up temperatures are achieved (e.g., coolant temperature, oxygen sensor temperature, choke-off temperature, catalyst operating temperature), large increases in HC and CO emissions and small decreases in fuel economy will occur. In addition, if future exhaust emission standards become more stringent, the apparent percentage emission increases associated with cold temperature operation will undoubtedly become more pronounced.

UNREGULATED EMISSIONS -- Because of the oxidation and reduction processes of the 3-way catalyst, various unregulated emissions may be formed in significant quantities. For example, the catalytic reduction process of reducing NO_x to N_2 also provides a mechanism for the formation of other reduced species, including COS, H_2S, NH_3, and HCN. The catalytic oxidation process of oxidizing HC and CO to carbon dioxide and water is also a mechanism for the formation of other oxidized species including SO_2, SO_4, and N_2O. Specific unregulated emissions will be analyzed and discussed in separate sections below. Figures 8-16, representing the individual bag 1, 2, and 3 and overall FTP unregulated emission rates, display both the range of emission rates observed and the calculated average emission rate. The range is depicted by a horizontal line and the average is depicted by a circle on the line.

A brief summary of the various pollutant Threshold Limit Values (TLVs) with their toxicity symptoms (16) is presented in Table 5. The TLVs were determined by OSHA (Occupational Safety and Health Administration) (17) and/or by the 1976 ACGIH (American Conference on Governmental Industrial Hygenists)(18), and the values here represent the maximum 8-hour work shift exposures they established. In the situation where no TLV has been established for a known toxic pollutant, one has been estimated by comparison with a similar compound. For example, the TLV for COS is estimated to be similar to H_2S's TLV of 10 ppm. NO_x composition was assumed to be 50% NO_2 and 50% NO and its TLV estimated to be 15 ppm. No TLV has been established for N_2O or HC (other than benzene) since neither has specifically been defined as a toxic pollutant. The TLV values listed in Table 5 use the minimum of the OSHA or ACGIH values. Comparison of these values with specific emission rates are discussed below.

NH_3 -- A toxic gas, NH_3, is formed in the exhaust by the reduction of nitrogen. Overall FTP NH_3 emissions, depicted in Figure 8, were greatest for the malfunctioning Buick Century, which has an average FTP NH_3 emission rate of 212.36 mg/mile at ambient temperature. For the vehicles with functioning emission control systems, subambient temperature operation maximized NH_3 emissions during bag 1 vehicle operation. For example, bag 1 emissions for the Lincoln at 58°F averaged 225.38 mg/mile versus 40.21 mg/mile at 78°F; for the Ford Pinto at 61°F they averaged 64.97 mg/mile versus 4.56 mg/mile at 78°F; and for the Chevrolet Caprice at 60°F, they averaged 100.77 mg/mile versus 64.48 mg/mile at 81°F. Minimum NH_3 emissions for the Lincoln, Ford, and Chevrolet occurred during bag 2 vehicle operation at ambient temperature. Overall FTP NH_3 emission rates followed the pattern: Buick >> Chevrolet ~ Lincoln > Ford.

The maximum observed NH_3 emission rate was 322.47 mg/mile during bag 1 operation of the Lincoln Continental at 58°F. This corresponds to an undiluted exhaust concentration of 102 mg/m^3, 5.6 times the TLV established for NH_3 (18 mg/m^3). The maximum observed overall FTP NH_3 emission rate was 224.68 mg/mile at 78°F for the Buick Century, which corresponds to an undiluted exhaust concentration of 56 mg/m^3, 3.1 times the NH_3 TLV.

HCN -- Formed in the exhaust by the catalytic reduction of nitrogen or nitrogen oxides, HCN is also a very toxic gas. Overall FTP HCN emissions (see Figure 9) were greater for the Ford Motor Company vehicles than for the General Motors vehicles at the subambient temperatures (average of 4.7 versus 1.3 mg/mile). The maximum emissions occurred during

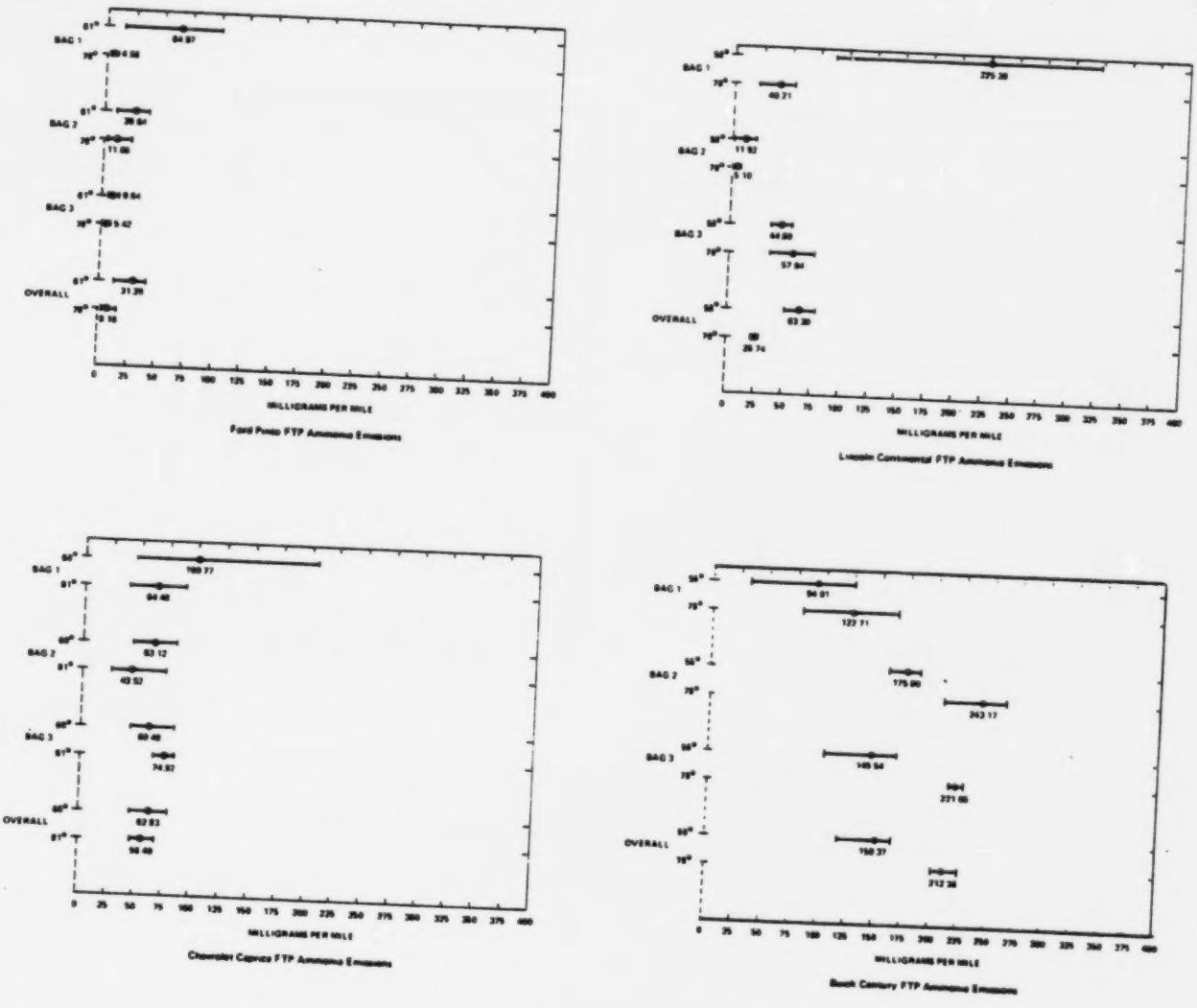

Fig. 8 - Ammonia emissions

bag 1 vehicle operation. HCN emissions increased significantly during subambient temperature operation. For example, bag 1 emissions for the Lincoln at 58°F averaged 22.53 mg/mile versus 1.02 mg/mile at 78°F; for the Pinto at 61°F averaged 19.59 mg/mile versus 2.30 mg/mile at 78°F; for the Chevrolet at 60°F averaged 6.28 mg/mile versus 2.03 mg/mile at 81°F; and for the Buick at 55°F averaged 2.72 mg/mile versus 2.53 mg/mile at 78°F. The pattern for HCN bag 1 and overall FTP emissions was Lincoln ~ Pinto >> Chevrolet ~ Buick. It should be noted that although the Buick had the malfunctioning emission control system, its HCN emission rates were among the lowest observed.

The maximum observed HCN emission rate was 38.02 mg/mile during bag 1 at 61°F for the Ford Pinto. This emission rate corresponds to an undiluted exhaust concentration of 16 mg/m^3, 1.5 times the TLV established for HCN (11 mg/m^3). The maximum observed overall FTP HCN emission rate was 8 mg/mile at 61°F for the Ford Pinto, which corresponds to an undiluted exhaust concentration of 2 mg/m^3, 0.2 times the HCN TLV.

N_2O -- Also known as laughing gas and commonly used as an anesthetic in medical and dental procedures, N_2O is formed in the exhaust by the catalytic partial oxidation of nitrogen. Although presently defined as nontoxic, N_2O emissions are of concern because of their potential effect on the atmospheric ozone layer and their potential for causing birth defects (19). N_2O emissions, depicted in Figure 10, were greatest for the Buick Century at subambient temperatures in bags 2 and 3 and overall FTP emissions.

Fig. 9 - Hydrogen cyanide emissions

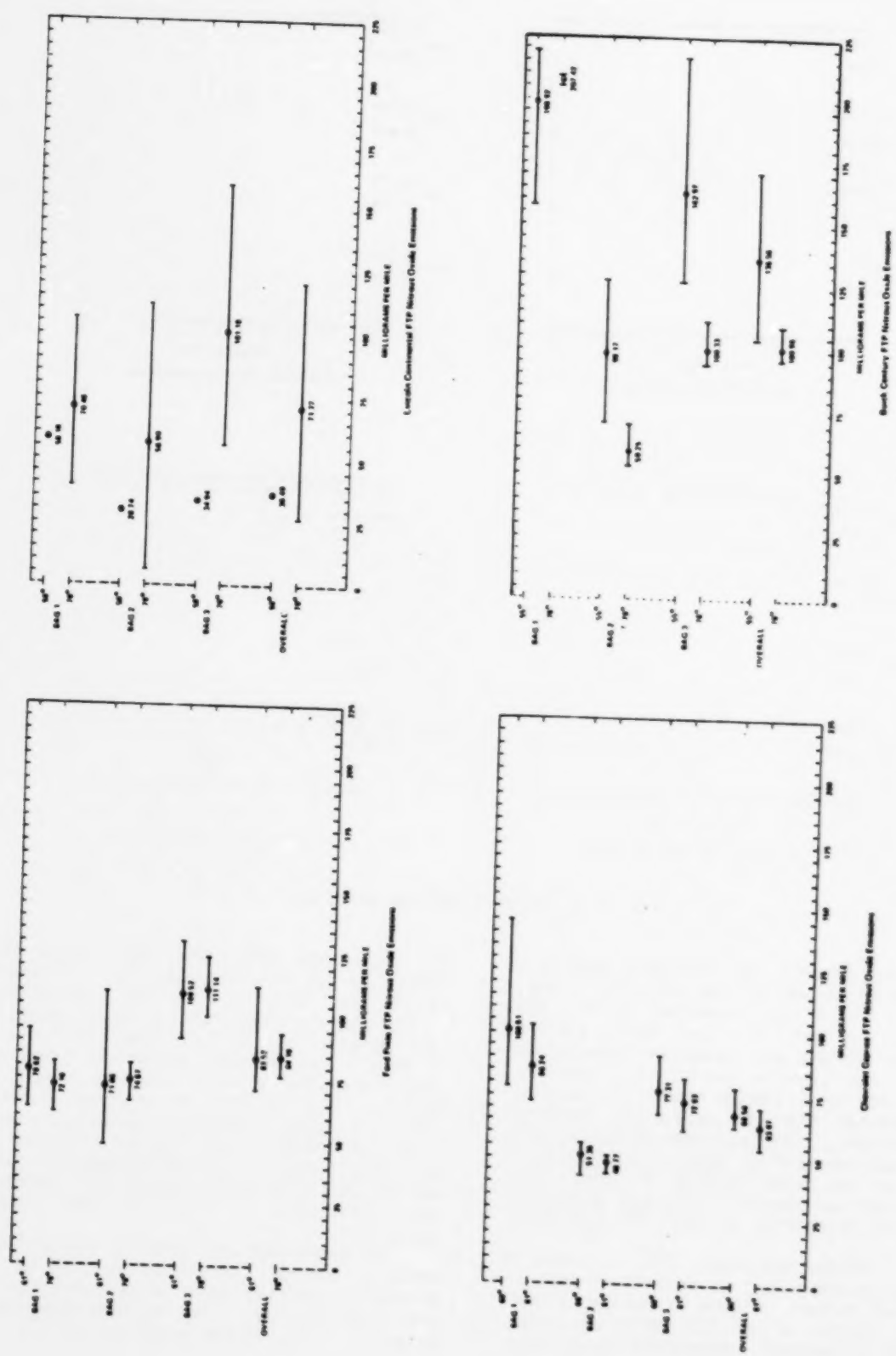

Fig. 10 - Nitrous oxide emissions

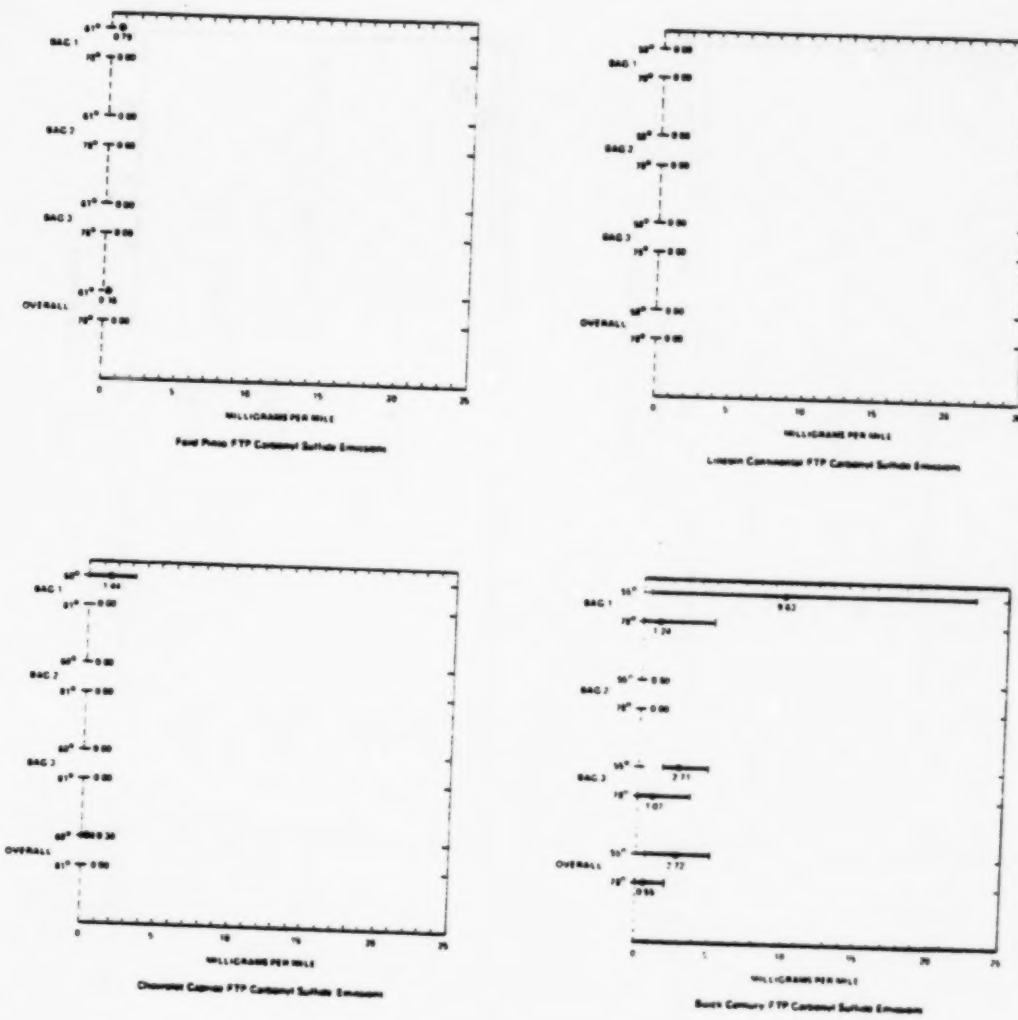

Fig. 11 - Carbonyl sulfide emissions

With the Ford, Lincoln, and Chevrolet vehicles, there appeared no definitive emissions trend. For example, with the Chevrolet Caprice and Ford Pinto, N_2O emissions were quite similar for both the ambient and subambient temperature tests; for the Lincoln Continental, however, the N_2O ambient temperature emissions appeared greater than the subambient temperature emissions. The maximum observed N_2O emission rate was 219.53 mg/mile during bag 1 operation of the Buick Century at 55°F. The maximum observed overall FTP N_2O emission rate was 171.24 mg/mile at 55°F for the Buick Century.

COS -- Another toxic gas, COS, is formed in the exhaust by the reduction or partial combustion of fuel sulfur. Figure 11 indicates that there was little or no COS emission under ambient or subambient temperature conditions for either the Ford Pinto, the Lincoln Continental, or the Chevrolet Caprice. For example, no COS was detected from the Lincoln Continental in any test; COS in small quantities (<0.8 mg/mile) was emitted from the Ford Pinto in bags 1 and 3 under subambient temperature conditions; and a small quantity of COS (3.0 mg/mile) was emitted during bag 1 vehicle operation under subambient temperature conditions for the Chevrolet Caprice. The vehicles with the functional emission control systems emitted COS only during subambient temperature operation, most of it during bag 1 vehicle operation.

The Buick Century, with its malfunctioning emission control system running rich of stoichiometry, emitted quite a bit more COS than any other vehicle. The maximum observed COS emission rate, which occurred during bag 1

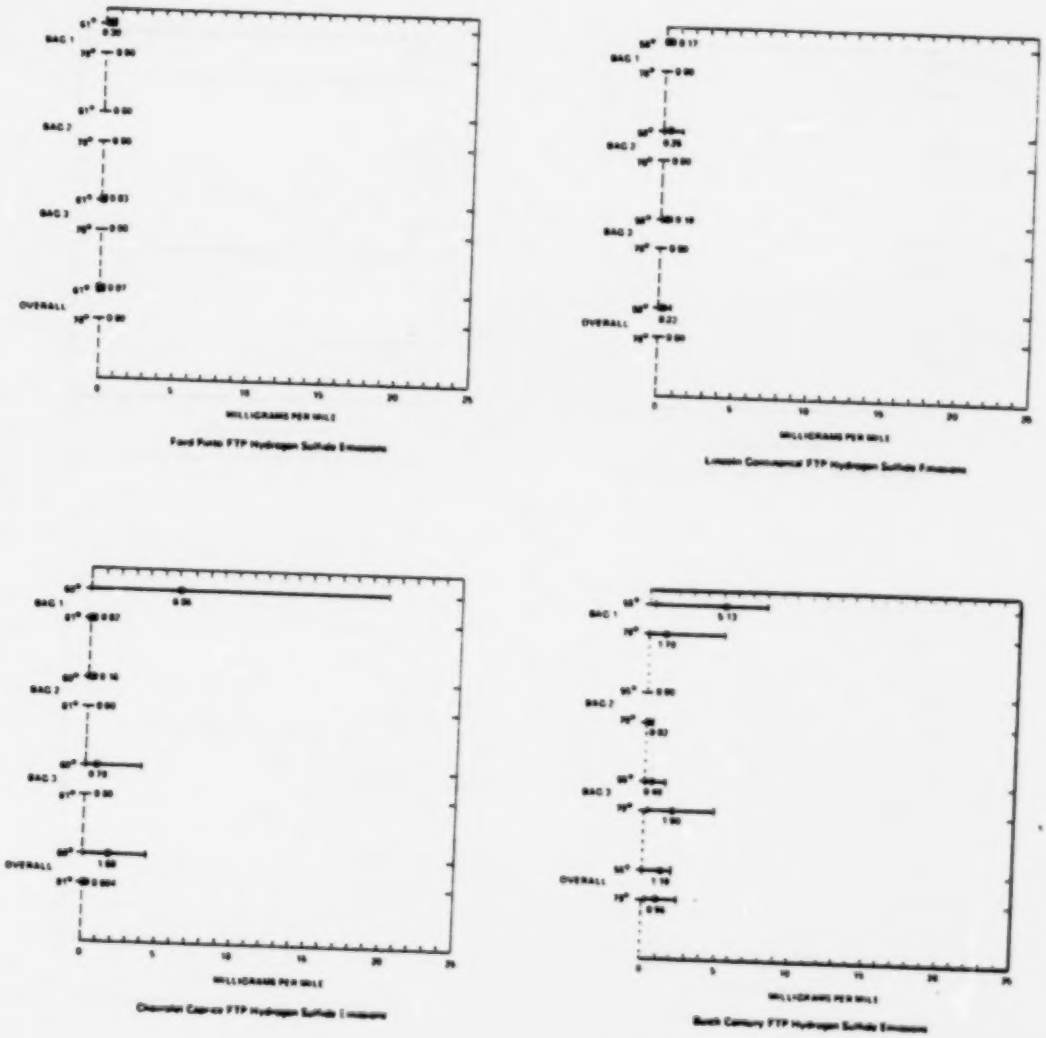

Fig. 12 - Hydrogen sulfide emissions

vehicle operation under subambient temperature conditions, was 22.08 mg/mile corresponding to an undiluted exhaust concentration of 7 mg/m^3, 0.28 times the TLV estimated for COS (25 mg/m^3). No COS was detected in bag 2 and only a small quantity in bag 3 (<5 mg/mile). The maximum observed overall FTP COS emission rate was 5.0 mg/mile, which corresponds to an undiluted exhaust concentration of 1 mg/m^3, 0.04 times the COS estimated TLV.

The overall pattern for COS emissions was Buick >> Chevrolet ~ Ford ~ Lincoln. Subambient temperature operation increased COS emissions in all cases. The reasons for this are two-fold. First, the winter (subambient) fuel sulfur content is 1.8 times greater than the summer (ambient) fuel sulfur content; hence, under identical vehicle operating conditions, sulfur-related emissions from the winter fuel theoretically should be 1.8 times more than the summer fuel. Second, under subambient temperature operations, both the vehicle and catalyst are cold and under a rich (i.e., choke "on") operating condition. Therefore, reduction and/or partial combustion processes dominate until the vehicle and catalyst are warm. More COS is emitted from the winter fuel under subambient temperature conditions than can be adequately explained by the first reason alone; both reasons must be taken into consideration to account for the increase.

H_2S -- A toxic, malodorous gas H_2S is formed in the exhaust by the reduction of fuel sulfur. Its characteristic rotten egg smell has one of the lowest odor thresholds known, less than 5 ppb or 0.007 mg/m^3 (20), which is three orders of magnitude less than the H_2S TLV of 10 ppm or 14 mg/m^3. In fact,

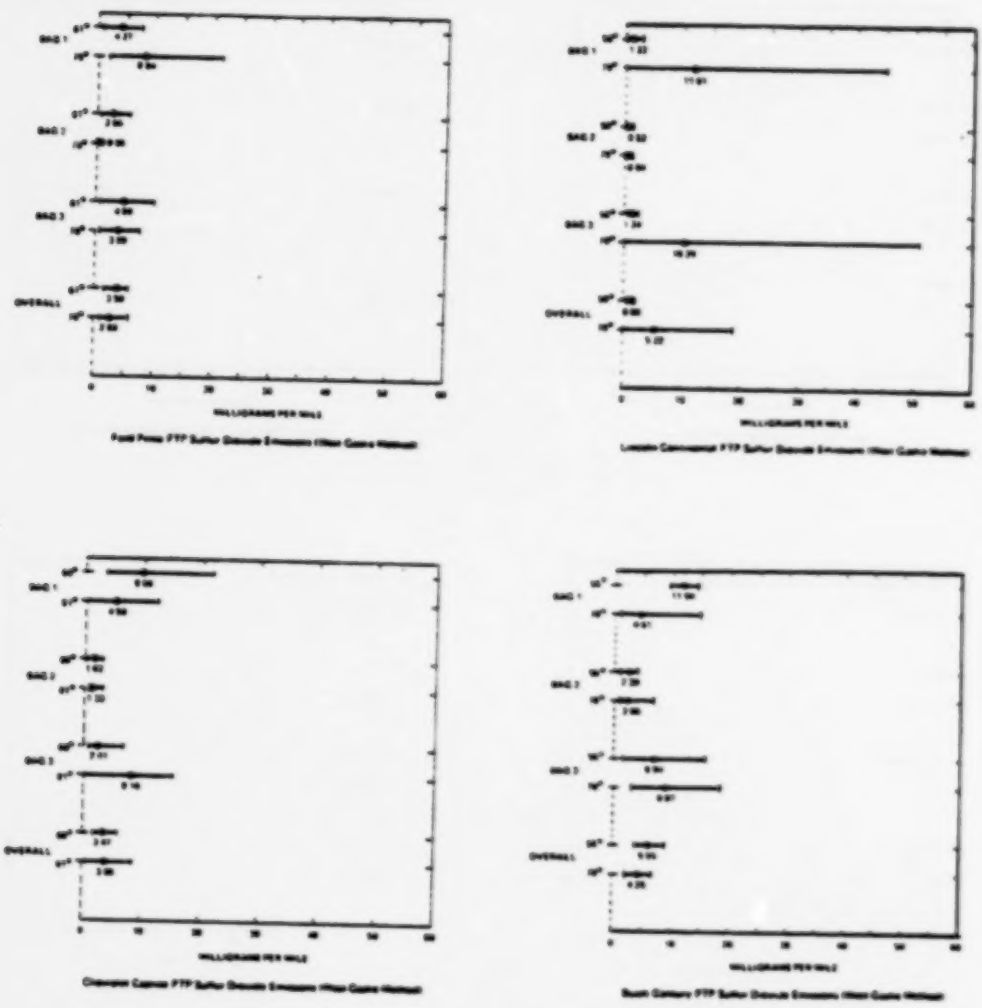

Fig. 13 - Sulfur dioxide emissions by West-Gaeke method

its odor threshold is so low, that it may be possible to smell H_2S under low exhaust dilution conditions (e.g., idle) without actually being able to measure it (minimum analytical H_2S detection level is~10 ppb). H_2S (see Figure 12) like COS, is emitted mostly in bag 1 under subambient temperature conditions. Little or no H_2S was detected from the Ford Pinto or Lincoln Continental in any test. The Chevrolet Caprice emitted the maximum H_2S in bag 1 under subambient temperature conditions. Its emission rate was 20.07 mg/mile, which corresponds to an undiluted exhaust concentration of 6 mg/m^3, 0.42 times its TLV (14 mg/m^3). The amounts of H_2S detected in the other bags were negligible. The maximum observed overall FTP H_2S emission rate was 4.21 mg/mile for the Chevrolet Caprice under subambient temperature conditions, which corresponds to 1 mg/m^3, 0.07 times the TLV.

For the Buick Century, the emission of H_2S, ~1 mg/mile, did not vary substantially with temperature. Overall H_2S emissions followed the pattern Chevrolet ~ Buick >> Lincoln ~ Pinto.

SO_2 -- A toxic gas formed in the exhaust by the combustion of fuel sulfur, SO_2 is highly irritating and almost irrespirable, with an odor threshold of ~5 ppm. Three different analytical methods were used to measure SO_2: the West-Gaeke (spectrophotometric) method, ion chromatography, and the electrochemical (microcoulometric titration) method. Of the three methods, only the electrochemical method provided real time response.

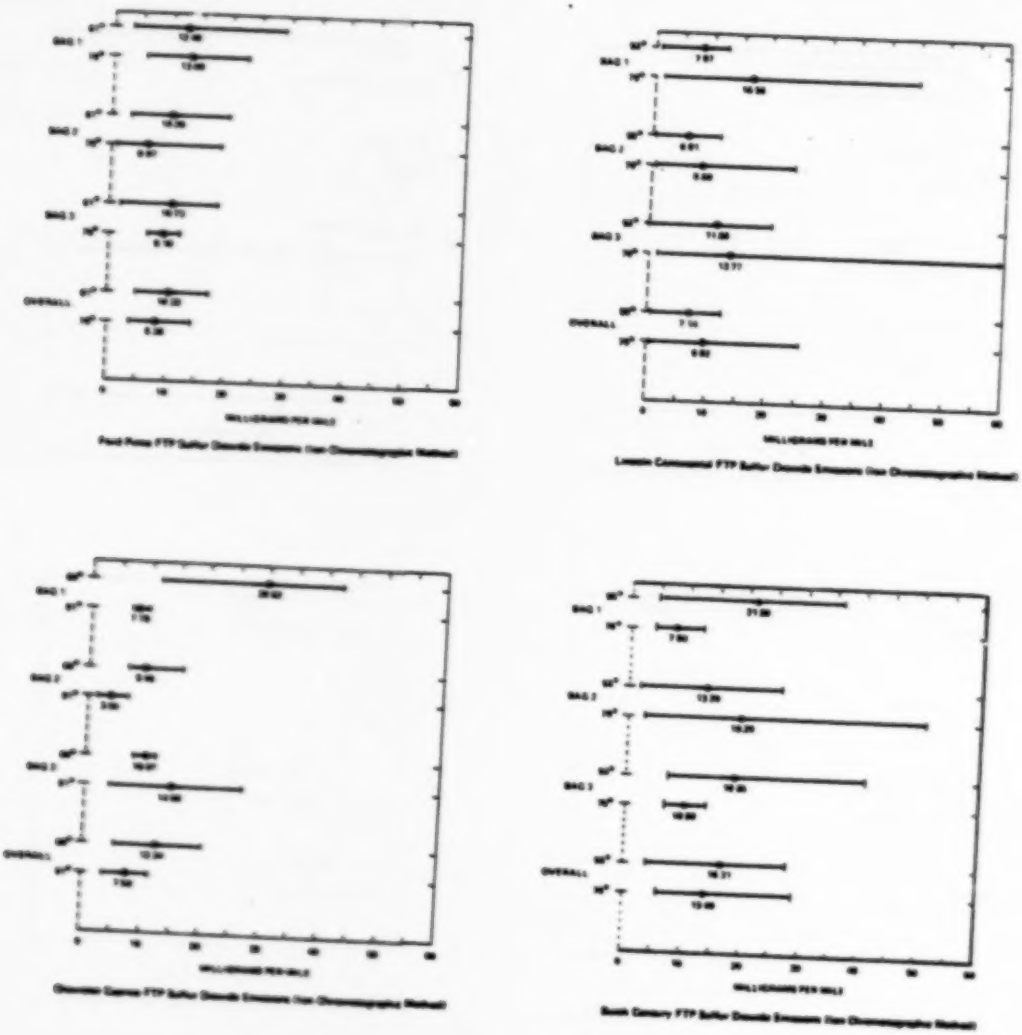

Fig. 14 - Sulfur dioxide emissions by ion chromatography method

The other two methods used impingers for individual bag sampling and provided integrated responses. All three methods were qualified by injecting known concentrations of SO_2 into the dilution tunnel and measuring SO_2 simultaneously by all three test procedures. The results of the injection experiments agreed to within 10%. Automotive testing of the three methods for measuring SO_2 with a non-catalyst vehicle indicated agreement within 25% of each other. However, during the 3-way catalyst vehicle tests, it became apparent that none of the results of the three methods agreed very well with each other. It was observed that the values of SO_2 by West-Gaeke (Figure 13) were less than the values obtained by electrochemistry (Figure 15) which, in turn, were less than the values obtained by ion chromatography (Figure 14). The reasons for the apparent disagreements are still under study. Among the possible reasons are: artifact formation; sample line contamination or water condensation due to various changes in SO_2 sample line configurations; reagent and/or sample contamination; and the possibility of poor SO_2 selectivity by one or more of the analytical methods. Nevertheless, the general trends in SO_2 emissions as determined by the three analytical procedures are in good agreement even though the actual emission rates differ. Consequently, SO_2 emissions will be discussed by using SO_2 by ion chromatography (Figure 14) as the representative "upper limit" method (i.e., SO_2 determination by the ion chromatographic procedure gave the maximum or "upper limit" results).

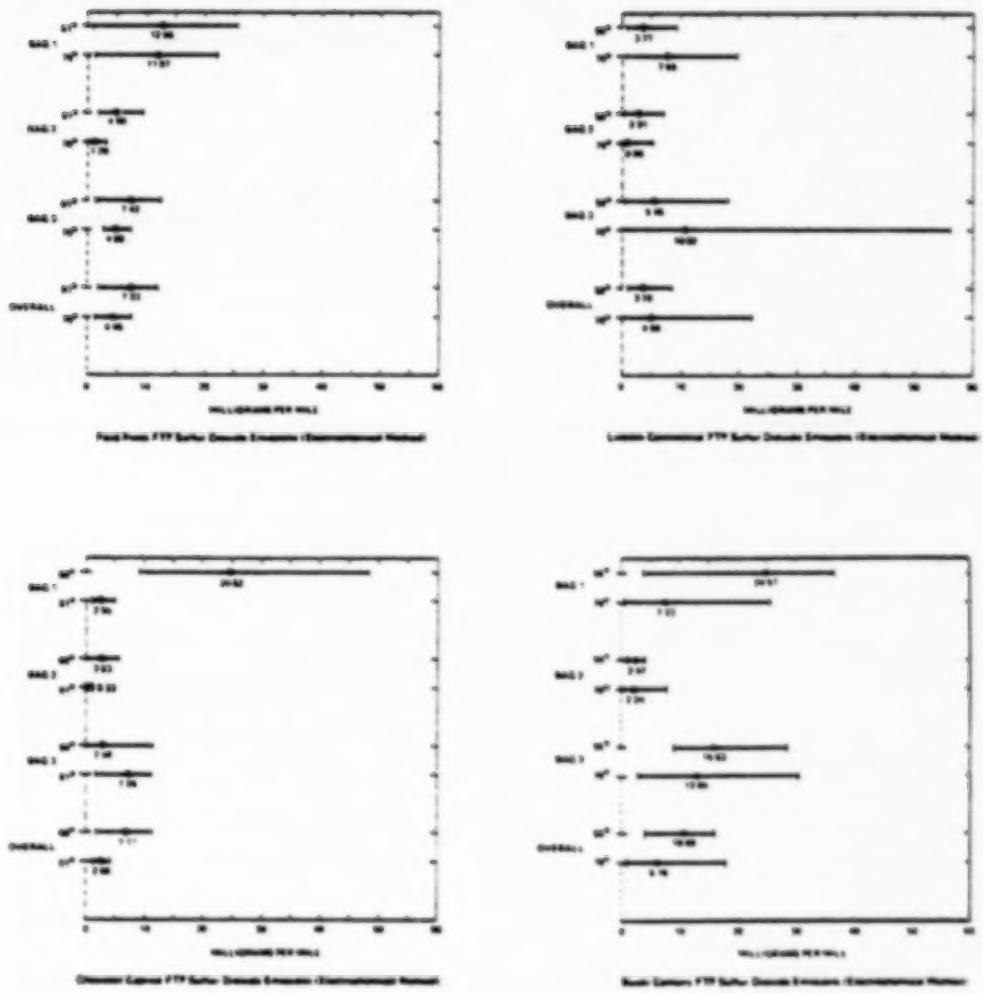

Fig. 15 - Sulfur dioxide emissions by electo-chemical method

SO_2 was emitted from all vehicles during bags 1, 2, and 3 of the FTP under both ambient and subambient temperature conditions. There was no pronounced difference or trend between overall FTP SO_2 emissions at either ambient or subambient temperature. For example, for the Ford, Chevrolet, and Buick, overall FTP subambient emissions were greater than FTP ambient emissions; for the Lincoln Continental, the reverse is true. In general, overall FTP SO_2 emissions were slightly greater from the General Motors vehicles than from the Ford Motor Company vehicles (12.4 versus 9.0 mg/mile overall FTP average). The maximum observed rate was 59.42 mg/mile during bag 3 operation of the Lincoln Continental under ambient temperature conditions. This corresponds to an undiluted exhaust concentration of 22 mg/m^3, 1.7 times the SO_2 TLV (13 mg/m^3). The maximum observed overall FTP SO_2 emission rate was 28.84 mg/mile for the Buick Century under ambient temperature conditions, corresponding to an undiluted exhaust concentration of 7 mg/m^3, 0.54 times the TLV.

A somewhat unexpected result of this study is that, although the fuel sulfur content at subambient temperatures is 1.8 times greater than at ambient temperatures, the SO_2 emissions are not correspondingly increased. In most cases, the subambient results were greater than the ambient results, but not by the predicted amount. Since the winter fuel was run first, it is possible that the catalyst's SO_2/SO_4 storage/release mechanism conditioned the catalyst to higher sulfur levels.

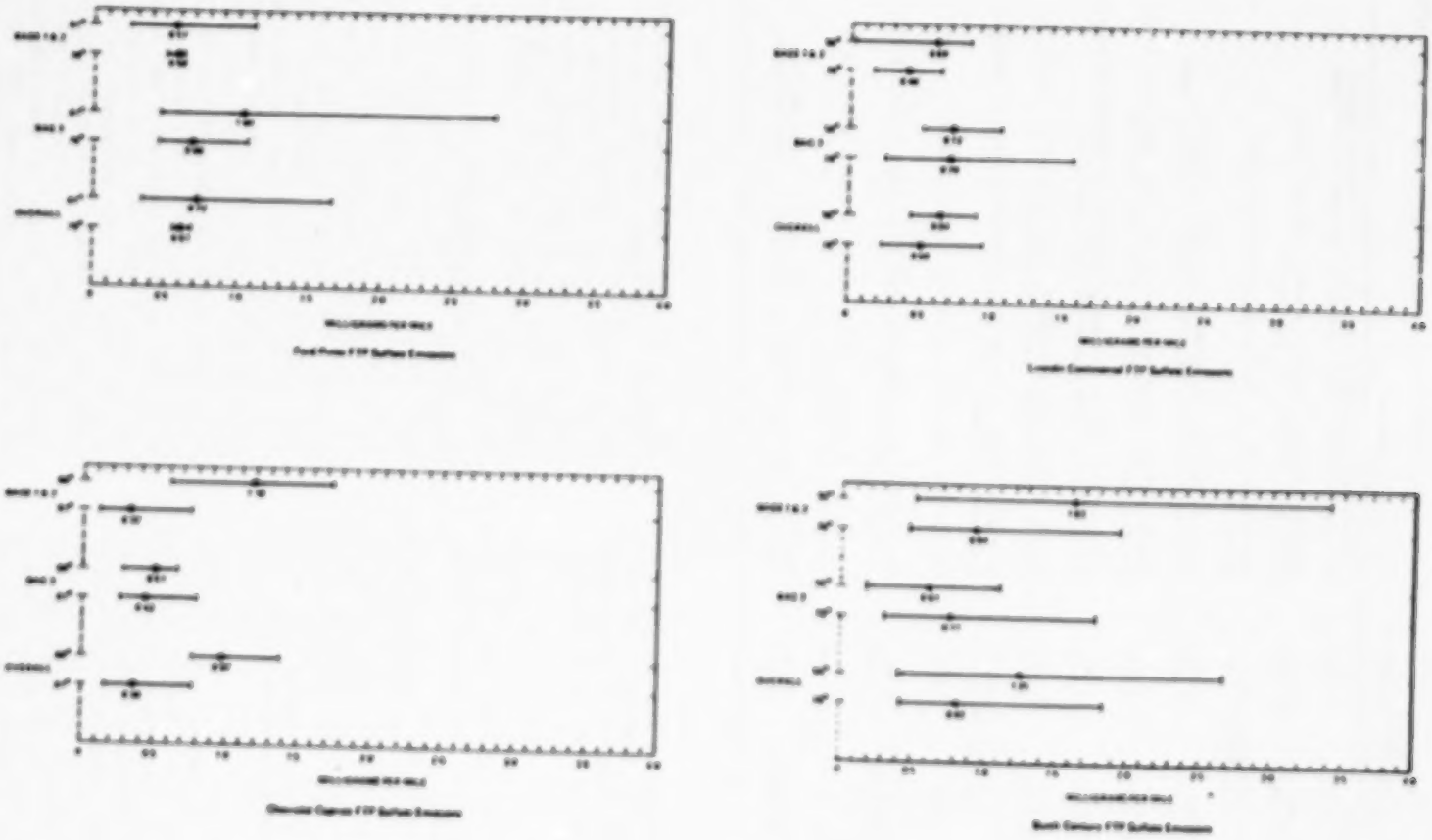

Fig. 16 - Sulfate emissions

Table 6 - Pollutants, TLVs, and Toxicity Symptoms

Pollutant	TLVs (ppm)	TLVs (mg/m³)	Toxicity Symptoms
Ammonia NH_3	50ppm	25 ppm 18 mg/m³	Pulmonary edema, breathing difficulty, skin irritation, mucous membrane irritation, visual disorders, gastrointestinal upset.
Carbon Monoxide CO	50 ppm 58 mg/m³	50 ppm 58 mg/m³	Headache, dizziness, vomiting, nausea, tinnitus (ringing of the ear), perspiration, systemic pain.
Carbonyl Sulfide COS	Estimated 10 ppm Estimated 25 mg/m³		Respiratory tract irritation, central nervous system depression.
Hydrogen Cyanide HCN	10 ppm 11 mg/m³	10 ppm 11 mg/m³	Dizziness, headache, gastrointestinal upset, difficult breathing, palpitation, respiratory arrest, convulsions, death.
Hydrogen Sulfide H_2S	20 ppm 28 mg/m³	10 ppm 14 mg/m³	Adversely affects mucous membranes in eyes, nose, and throat; causes pulmonary edema, gastrointestinal upset, and convulsions.
Nitrogen Dioxide NO_2	5 ppm 10 mg/m³	5 ppm 10 mg/m³	Eye and skin irritation, asthmatic breathing, inflammation of respiratory tract, emphysema, gastrointestinal upset, convulsions.
Nitric Oxide NO	25 ppm 31 mg/m³	25 ppm 31 mg/m³	Fatigue, nausea, chocing, headache, inability to breath deeply, loss of appetite, constipation, general body weakness.
50% NO_2 - 50% NO NO_x	Estimated 15 ppm Estimated 20 mg/m³		Combination of NO_2 and NO effects: respiratory tract inflammation, gastrointestinal upset, fatigue.
Nitrous Oxide N_2O	None	None	Anesthetic by inhalation; possibility of birth defects.
Sulfur Dioxide SO_2	5 ppm 13 mg/m³	5 ppm 13 mg/m³	Respiratory tract inflammation, chest pain, cough, nausea, fatigue, eye irritation, burning of skin.
Sulfuric Acid H_2SO_4	--	0.25 ppm 1 mg/m³	Eye and skin irritation, shock, vomiting of blood, perforation of gastrointestinal tract.
Benzene C_6H_6	10 ppm 32 mg/m³	10 ppm 32 mg/m³	Euphoria, dizziness, narcosis; central nervous system depression, respiratory and gastrointestinal irritation; possible carcinogen.

Thus, when testing switched to the summer fuel with the lower fuel sulfur content, the catalyst still retained the "memory" of the higher sulfur fuel and released SO_2 accordingly. This possibility may also help explain the SO_2 data scatter. At any rate, it would be almost impossible to achieve a fair sulfur balance in this type of testing due to the limited number of tests and the lack of long-term catalyst conditioning.

SO_4 -- When emitted in the form of sulfuric acid aerosol, SO_4 is toxic. It is formed by the catalytic oxidation of SO_2 to SO_3, which is then hydrated to form sulfuric acid (H_2SO_4). The amount of SO_4 formed is a function of the driving cycle (21), the fuel sulfur content, catalyst composition and activity, and the catalyst's SO_2/SO_4 storage/release capacity. All of the test vehicles emitted SO_4 in bags 1 and 2 (combined) and bag 3 of the FTP. Overall FTP SO_4 subambient temperature emission rates were greater than ambient temperature rates, but not by the amount predicted based on fuel sulfur content considerations alone (see SO_2 discussion). The General Motors vehicles emitted slightly more SO_4 than the Ford Motor Company vehicles. The maximum observed SO_4 emission rate was 3.42 mg/mile during bags 1 and 2 (combined) for the Buick Century under subambient temperature conditions. This corresponds to an undiluted exhaust concentration of 1 mg/m³, 1.0 times the TLV established for SO_4 (1 mg/m³). The maximum observed overall FTP SO_4 emission rate was 2.67 mg/mile for the Buick Century under subambient conditions, corresponding to an undiluted exhaust concentration of 1 mg/m³, 1.0 times the SO_4 TLV.

Total HC Composition -- Both the mass and composition of the tailpipe HC emissions are sensitive to temperature (Table 6). As previously discussed, tailpipe HC emission rates were greater at subambient temperatures than at ambient temperatures, from about 15% greater with the malfunctioning Buick to about 440% with the Lincoln Continental. The significance of these increases can be examined only when evaporative hydrocarbon emissions are considered concurrently; the evaporative emissions were not determined in this test program. However, decreased evaporative emissions would be expected under lower temperature conditions and this would lessen the significance of the increased tailpipe emissions to some extent. The compositional changes are in agreement with previously published data addressing the impact of catalyst technologies on tailpipe HC emissions (22, 23). Under subambient temperature conditions, the catalyst requires a longer time to achieve the proper light-off temperature; subsequently the exhaust

displays the characteristics of a non-catalyst vehicle's exhaust. The exhaust at subambient temperature has an increased relative fraction of olefinic hydrocarbons and a decreased relative fraction of methane and acetylene. Generally, the aromatic fraction would also be expected to increase at subambient temperature but this is not evident in this data because of the lower aromatic content of the winter grade test fuel. The fuel composition generally dominates the exhaust hydrocarbon composition for compounds of higher molecular weight than butane. The Buick data do not show the expected compostional trends because of the previously described emission control malfunction (i.e., running rich of stoichiometry). The Buick data do indicate, however, that due to this malfunction, significant quantities of benzene were emitted under both ambient and subambient temperature conditions. The maximum observed benzene FTP emission rate was 246.40 mg/mile and was obtained under ambient temperature conditions. This corresponds to an undiluted exhaust concentration of 61.45 mg/m^3 or 1.9 times the benzene TLV (32 mg/m^3).

RELATIVE TOXICITIES -- Comparisons of the maximum undiluted emission rates for both regulated and unregulated emissions to their respective TLVs are presented in Table 7 (for individual bag ratios) and Table 8 (for overall FTP ratios). Regulated emissions ratios are

Table 6 - Total Hydrocarbon Composition

Weight Percent of Total	Ford Pinto		Lincoln Continental		Chevrolet Caprice		Buick Century	
	Summer Fuel @ 78°F	Winter Fuel @ 62°F	Summer Fuel @ 78°F	Winter Fuel @ 58°F	Summer Fuel @ 81°F	Winter Fuel @ 60°F	Summer Fuel @ 78°F	Winter Fuel @ 55°F
Methane CH_4	30.0	18.3	33.6	18.5	24.9	17.6	22.4	21.2
Paraffins	67.9	57.0	67.2	58.0	59.6	56.9	54.3	58.4
Olefins	10.2	16.3	6.6	16.8	10.9	16.1	8.2	13.7
Aromatics	20.7	23.3	25.2	23.9	28.4	21.9	37.3	27.1
Benzene	3.1	4.3	6.0	4.2	7.2	4.5	15.4	10.1
Acetylene	1.2	3.2	1.0	1.3	1.1	5.1	0.4	0.8
Overall HC grams/mile	0.41	1.33	0.26	1.40	0.33	1.18	1.60	1.84

Table 7 - Approximate Ratio of Maximum Individual Bag Emission Rate (Undiluted) to TLV

Emission Type	Maximum observed emission rate for individual test phase in mg/mile	Equivalent maximum concentration in undiluted exhaust in mg/m^3	Threshold Limit Value (TLV) in mg/m^3	Ratio of equivalent maximum concentration to TLV
Regulated Emissions				
HC	5910	1862	--	--
CO	87640	27606	58	476
NOx	2320	767	20	38
Unregulated Emissions				
NH_3	322	102	18	5.6
HCN	38	16	11	1.5
N_2O	220	73	--	--
COS	22	7	25	0.28
H_2S	20	6	14	0.42
SO_2	59	22	1	1.7
SO_4	3	1	1	1

Table 8 - Approximate Ratio of Maximum FTP Emission Rate (Undiluted) to TLV

Emission Type	Maximum observed emission rate for overall FTP in mg/mile	Equivalent maximum concentration rate in undiluted exhaust in mg/m^3	Threshold Limit Value (TLV) in mg/m^3	Ratio of equivalent maximum concentration to TLV
Regulated Emissions				
HC	1810	452	--	--
CO	30960	7740	58	133
NO_x	1710	427	20	21
Unregulated Emissions				
NH_3	225	56	18	3.1
HCN	8	2	11	0.2
N_2O	171	43	--	--
COS	5	1	25	0.04
H_2S	4	1	14	0.07
SO_2	29	7	13	0.54
SO_4	3	1	1	1.0
C_6H_6	246	61	32	1.9

depicted in Figure 17 and unregulated emissions ratios in Figure 18. It should be noted that Tables 7 and 8 and Figures 17 and 18 reflect approximate ratios of the maximum observed undiluted (i.e., tailpipe concentration) pollutant emission rates to TLVs. It should also be noted that there are additional methods, other than the TLV comparison method, available for estimating or assessing concentrations based on either potential ecological effects or on predicted toxic levels for man (24).

Regulated emissions ratios (Figure 17) indicate that for undiluted exhaust concentrations, CO exceeds its TLV by a factor > 100 and NO_x exceeds its TLV by a factor > 10. The bag 1 CO ratio of 476 comes from the Lincoln Continental under subambient temperature conditions and the FTP CO ratio of 133 is from the Buick Century under subambient temperature conditions. The bag 1 NO_x ratio of 38 reflects the Buick Century operation under subambient temperature conditions and the FTP NO_x ratio of 21 reflects the Lincoln Continental operation under ambient temperature conditions.

To assess the concentration of CO and NO_x that a commuter might experience in a severe situation, a crowded expressway exposure case was developed and modeled using the Chock Gaussian line source model for pollution dispersion near roadways (25). This exposure case is defined as an area having high traffic flow, parallel wind, and neutral stability for a large percentage of the time. Traffic density, wind direction, and wind speed values used were taken from a Houston expressway study. If the maximum observed FTP CO and NO_x undiluted emission rates from Table 8 are inserted into this model, a CO commuter exposure concentration of ~5 mg/m^3 (0.09 times the CO TLV) and an NO_x commuter exposure concentration of ~0.3 mg/m^3 (0.015 times the NO_x TLV) are obtained. These exposure concentration levels represent approximate raw exhaust dilution ratios of 1500 to 1. If one were to simply assume a raw exhaust dilution ratio of 1000 to 1 to simulate a "worst case" exposure model for the individual test phase emission rates listed in Table 7, then a CO commuter exposure of ~27 mg/m^3 (0.48 times the CO TLV) and an NO_x commuter exposure of ~0.8 mg/m^3 (0.04 times the NO_x TLV) would be obtained.

Unregulated emission ratios, depicted in Figure 18, indicate that the undiluted bag 1 exhaust concentrations of HCN, SO_4, and SO_2 exceed their respective TLVs by factors less than 6. The HCN emissions ratio is from the Ford Pinto operation under subambient temperature conditions; the NH_3 ratio reflects the Lincoln Continental test under subambient

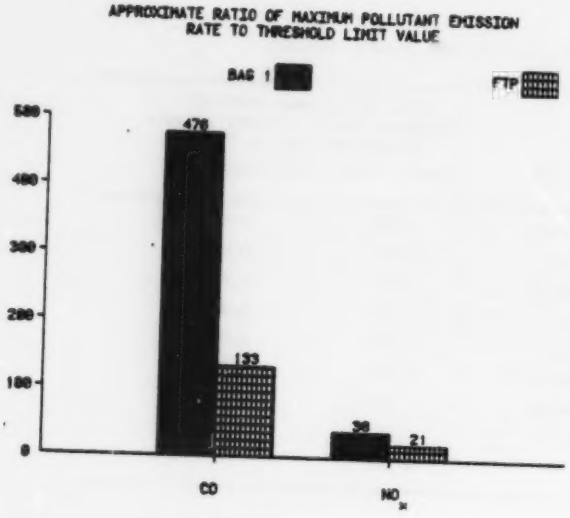

Fig. 17 - Regulated emissions ratio

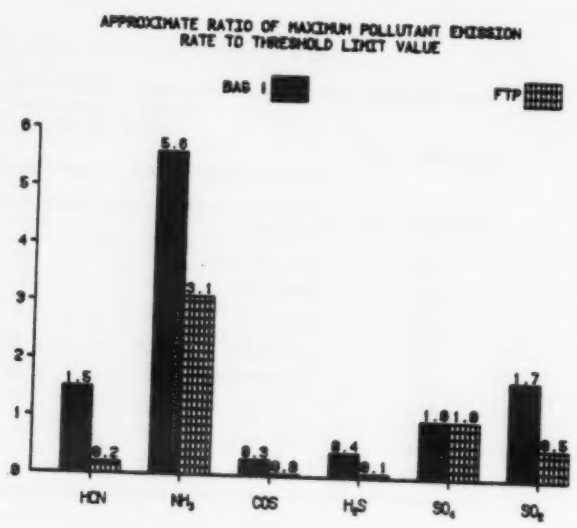

Fig. 18 - Unregulated emissions ratio

temperature conditions; the SO_4 ratio is from the Buick Century operation under subambient temperature conditions; and the SO_2 ratio reflects the Lincoln Continental test under ambient temperature conditions. Again, if one simply assumes a raw exhaust dilution ratio of 1000 to 1 to simulate a "worst case" exposure model for the individual test phase emission rates listed in Table 8, the NH_3 commuter exposure would be ~0.10 mg/m^3 (0.006 times the NH_3 TLV); an HCN commuter exposure would be ~0.016 mg/m^3 (0.002 times the HCN TLV); and SO_2 commuter exposure would be ~0.022 mg/m^3 (0.001 times the SO_2 TLV); and an SO_4 commuter exposure of ~0.001 mg/m^3 (0.001 times the SO_4 TLV).

The overall FTP unregulated raw exhaust emission ratios indicate that only NH_3, SO_4, and C_6H_6, all based on the Buick Century tests under ambient temperature conditions, exceed or equal their TLVs by factors of 3.1, 1.0, and 1.9, respectively. The other unregulated emissions, HCN, COS, H_2S, and SO_2, did not exceed their TLVs in FTP undiluted exhaust. If the maximum observed FTP NH_3, SO_4, and C_6H_6 undiluted emission rates from Table 8 are inserted into the aforementioned crowded expressway exposure situation, an NH_3 commuter exposure concentration of~0.04 mg/m^3 (0.002 times the NH_3 TLV), an SO_4 commuter exposure concentration of~0.001 mg/m^3 (0.001 times the SO_4 TLV), and a C_6H_6 commuter exposure concentration of~0.04 mg/m^3 (0.002 times the C_6H_6 TLV) are obtained, representing an approximate raw exhaust dilution ratio of 1500 to 1. Table 9 summarizes the relative toxicities of undiluted and diluted exhaust emissions and tabulates the relative commuter exposure to TLV ratio. It also shows which vehicle was the worst polluter under which temperature condition.

What all this means is that, based on a limited number of tests with four late model 3-way catalyst automobiles, subambient temperature operation significantly increased the regulated emissions of HC and CO and slightly increased the unregulated emissions of NH_3, HCN, SO_2, and SO_4. Based on the 8-hour TLV exposure criteria alone, CO is the most important pollutant to consider in terms of toxicity. TLV comparisons of the unregulated emissions indicate that none are released at concentrations that could be considered hazardous to the public. However, some important caveats concerning TLV exposure must be pointed out: continuous exposures of 24 hours rather than the 8-hour work day were not taken into consideration; and mutagenicity, carcinogenicity, cumulative, synergistic or indirect effects were also not considered.

CONCLUSIONS

1. HC and CO emissions were significantly higher during subambient temperature (48^0-67^{0}F) operation than during FTP temperature (68^0-86^{0}F) operation.

2. The cold transient bag 1 test phase (HC and CO) emissions are much more responsive to temperature reduction than bag 2 or bag 3 or the overall FTP. Almost all HC and CO emission increases observed at subambient temperature occur during bag 1 operation.

3. NO_x emissions are affected by ambient temperature changes. The degree to which

Table 9 - Relative Toxicities of Emissions in Undiluted and Diluted Exhaust

Emission Type	Ratios of undiluted exhaust concentration to TLV (Vehicle) Overall FTP - Individual Bag (Vehicle)					Ratio of maximum commuter exposure level (diluted exhaust concentrations) to TLV Overall FTP - Individual Bag		
CO	(S-Buick)	133	-	476	(S-Lincoln)	0.090	-	0.476
NO_x	(A-Lincoln)	21	-	38	(S-Buick)	0.015	-	0.038
NH_3	(A-Buick)	3.1	-	5.6	(S-Lincoln)	0.002	-	-.056
HCN	(S-Ford)	0.2	-	1.5	(S-Ford)	0.001	-	0.002
COS	(S-Buick)	0.04	-	0.28	(S-Buick)	0.001	-	0.001
H_2S	(S-Chevrolet)	0.07	-	0.42	(S-Chevrolet)	0.001	-	0.001
SO_2	(A-Buick)	0.54	-	1.0	(A-Lincoln)	0.001	-	0.001
SO_4	(S-Buick)	1.0	-	1.0	(S-Buick)	0.001	-	0.001
C_6H_6	(A-Buick)	1.9				0.002		

A = Ambient temperature range result (68° - 82°F).

S = Subambient temperature range result (48° - 67°F).

they are affected is not nearly as great as that to which HC and CO are affected and appears to be a function of emission control technology.

4. Fuel economy decreased under subambient temperature operation by approximately 0.4%/°F. Consequently, if fuel economy and regulated exhaust emissions are to be modeled, then the data from the FTP should be adjusted to reflect both seasonal and geographical ambient temperature influences.

5. CO and NO_x undiluted exhaust (tailpipe) concentrations exceed the TLVs established or estimated by OSHA and/or ACGIH by a significant factor. However, both CO and NO_x are diluted below the TLV in maximized commuter exposure situations in the examined temperature ranges.

6. The unregulated emissions of NH_3, HCN, COS, H_2S, SO_2 and SO_4 were greater during subambient temperature operation than during FTP temperature operation. Cold transient bag 1 test phase emissions were more responsive to temperature decrease than bag 2 or bag 3 or the overall FTP.

7. Of the unregulated emissions, NH_3, HCN, COS, H_2S, SO_2, SO_4 and C_6H_6, only the undiluted exhaust concentration of NH_3, HCN, SO_2, SO_4, and C_6H_6 exceeded the TLVs established or estimated by OSHA and/or ACGIH by very small factors.

All of the unregulated emissions are diluted considerably below the TLV in maximized commuter exposure situations. Hence, the results of this investigation indicate that none of the unregulated emissions are emitted at concentrations that could be considered a public health risk using the 8-hour TLV comparison methodology.

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Appendix A - Sampling and Analysis Methodology for Exhaust Emissions

Emission Type		Sample Type	Method of Analysis
HC	Regulated	Bag	Flame ionization detector
CO, CO_2	Emissions	Bag	Non-dispersive infrared
NO_x		Bag	Chemiluminescence
Detailed Hydrocarbons [i.e., C_6H_6 (Benzene), etc.]		Bag	Gas chromatograph with flame ionization detector
Sulfur dioxide (SO_2 #1)		Impinger	West-Gaeke method, tetrachloromercurate complex with spectrophotometric detection
(SO_2 #2)		Impinger	Ion chromatograph
(SO_2 #3)		Real time - diluted exhaust	Electrochemical: microcoulometric titration
Sulfate ($SO_4^=$)		Filter	Ion chromatograph
Carbonyl sulfide (COS)		Bag	Gas chromatograph with flame photometric detector

Appendix A - Sampling and Analysis Methodology for Exhaust Emissions

Emission Type	Sample Type	Method of Analysis
Hydrogen sulfide (H_2S)	Impinger	Methylene blue derivative with spectrophotometric detection
Ammonia (NH_3)	Impinger	Ion chromatograph
Nitrous Oxide (N_2O)	Bag	Gas chromatograph with electron capture detector
Hydrogen cyanide (HCN)	Impinger	Cyanogen chloride and pyridine-pyrazolone complex with spectrophotometric detection

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